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(54) **ELECTROLYTIC PROCESS FOR REMOVING A SUBSTANCE FROM SOLID COMPOUNDS**

**ELEKTROLYTISCHES VERFAHREN ZUR ENTFERNUNG EINES STOFFES VON FESTEN
VERBINDUNGEN**

PROCEDE ELECTROLYTIQUE D'ELIMINATION D'UNE SUBSTANCE DE COMPOSES SOLIDES

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Description

Field of Invention

[0001] This invention relates to a method for reducing the level of substances in solid metal compounds and semi-metal compounds. In addition, the method relates to the direct production of metals and semi-metals from their compounds.

Background to the Invention

[0002] Many metals and semi-metals form oxides. For example, titanium, zirconium and hafnium are highly reactive elements and when exposed to oxygen-containing environments rapidly form an oxide layer, even at room temperature. This passivation is the basis of their outstanding corrosion resistance under oxidising conditions. However, this high reactivity has attendant disadvantages which have dominated the extraction and processing of these metals.

[0003] The high reactivity of titanium and other Group IVA elements extends to reaction with refractory materials such as oxides, carbides etc. at elevated temperatures, again contaminating and embrittling the basis metal. This behaviour is extremely deleterious in the commercial extraction, melting and processing of the metals concerned.

[0004] Typically, extraction of a metal from a metal oxide is achieved by heating the oxide in the presence of a reducing agent (the reductant). The choice of reductant is determined by the comparative thermodynamics of the oxide and the reductant, specifically the free energy balance in the reducing reactions. This balance must be negative to provide the driving force for the reduction to proceed.

[0005] The reaction kinetics are influenced principally by the temperature of reduction and additionally by the chemical activities of the components involved. The latter is often an important feature in determining the efficiency of the process and the completeness of the reaction. For example, it is often found that although a reduction should in theory proceed to completion, the kinetics are considerably slowed down by the progressive lowering of the activities of the components involved. In the case of an oxide source material, this results in a residual content of oxygen (or another element that might be involved) which can be deleterious to the properties of the reduced metal, for example, in lower ductility, etc. This frequently leads to the need for further operations to refine the metal and remove the final residual impurities, to achieve high quality metal.

[0006] Because the reactivity of Group IVA elements is high, and the deleterious effect of residual impurities serious, extraction of these elements is not normally carried out from the oxide, but following preliminary chlorination, by reducing the chloride. Magnesium or sodium are often used as the reductant. In this way, the dele-

rious effects of residual oxygen are avoided. This inevitably leads, however, to higher costs which make the final metal more expensive, which limits its application and value to a potential user.

[0007] In addition to titanium, a further metal of commercial interest is Germanium, which is a semi-conducting metalloid element found in Group IVA of the Periodic Table. It is used, in a highly purified state, in infra-red optics and electronics. Oxygen, phosphorus, arsenic, antimony and other metalloids are typical of the impurities which must be carefully controlled in Germanium to ensure an adequate performance. Silicon is a similar semiconductor and its electrical properties depend critically on its purity content. Controlled purity of the parent silicon or germanium is fundamentally important as a secure and reproducible basis, onto which the required electrical properties can be built up in computer chips, etc.

[0008] US Patent 5,211,775 discloses the use of calcium metal in the liquid or vapour phase to deoxidise titanium. Okabe, Oishi and Ono (Met. Trans B. 23B (1992):583, have used a calcium-aluminium alloy to deoxidise titanium aluminate. Okabe, Nakamura, Oishi and Ono (Met. Trans B. 24B (1993):449) deoxidised titanium metal initially containing up to 1400 ppm dissolved oxygen. Titanium samples were immersed in a calcium chloride melt and voltages of more than 2.5V applied between the titanium and a carbon anode. The authors suggest that deoxidation is due to an increase of Ca activity and a decrease of CaO activity around the cathode surface. Okabe, Devra, Oishi, Ono and Sadoway (Journal of Alloys and Compounds 237 (1996) 150) have deoxidised yttrium using a similar approach, suggesting the same mechanism as proposed by Okabe, Nakamura, Oishi and Ono.

[0009] Ward *et al*, Journal of the Institute of Metals (1961) 90:6-12, describes an electrolytic treatment for the removal of various contaminating elements from molten copper during a refining process. The molten copper is treated in a cell with barium chloride as the electrolyte. The experiments show that sulphur can be removed using this process. However, the removal of oxygen is less certain, and the authors state that spontaneous non-electrolytic oxygen loss occurs, which may mask the extent of oxygen removal by this process. Furthermore, the process requires the metal to be molten, which adds to the overall cost of the refining process. The process is therefore unsuitable for a metal such as titanium which melts at 1660°C, and which has a highly reactive melt.

Summary of Invention

[0010] The invention provides a method for removing a substance from a solid metal compound or semi-metal compound, and a method for forming an alloy, as defined in the appended independent claims to which reference should now be made. Preferred or advanta-

geous features of the invention are set out in dependent subclaims.

[0011] In a preferred embodiment, the present invention may thus advantageously provide a method for removing a substance (X) from a solid compound (M¹X) between the substance and a metal or semi-metal (M¹). In the embodiment, an electrode comprising the solid compound is fabricated and contacted with a melt, or electrolyte (M²Y), comprising a fused salt or a mixture of salts, including one or more cations (M²) and one or more anions (Y). A potential is then applied to the electrode, the potential being lower than a deposition potential for the cation (M²), or the lowest deposition potential for any of the cations (M²), at a surface of the electrode and such that the substance (X) dissolves in the electrolyte.

[0012] In the method of the invention, electrolysis preferably occurs with a potential below the decomposition potential of the electrolyte.

[0013] In a preferred embodiment, the invention may be used to remove the oxygen from a metal oxide.

[0014] The invention may be used to electrolytically decompose oxides of elements such as titanium, uranium, magnesium, aluminium, zirconium, hafnium, niobium, molybdenum, neodymium, samarium and other rare earths.

[0015] In another embodiment, a further metal compound or semi-metal compound (M^NZ) may be present, and the electrolysis product may be an alloy of the metallic elements.

[0016] When mixtures of oxides are reduced, an alloy of the reduced metals will form.

[0017] If a mixture of oxides is used, the cathodic reduction of the oxides will cause an alloy to form.

[0018] According to one embodiment of the invention, M¹X is an insulator and is used in contact with a conductor. Alternatively, M¹X may be a conductor and be used as the cathode.

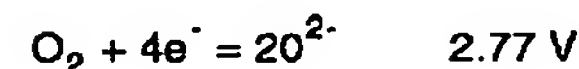
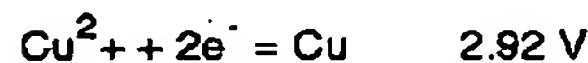
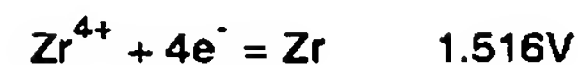
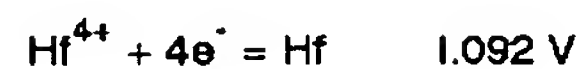
[0019] For example a metal oxide compound should show at least some initial metallic conductivity or be in contact with a conductor.

[0020] In a preferred embodiment, M² may be any of Ca, Ba, Li, Cs or Sr and Y is Cl.

[0021] In a further preferred embodiment, X is any of O, S, C or N.

[0022] In a still further preferred embodiment, M¹ is any of Ti, Si, Ge, Zr, Hf, Sm, U, Al, Mg, Nd, Mo, Cr, Nb, or any alloy thereof.

[0023] In principle, other cathodic reactions involving the reduction and dissolution of metalloids other than oxygen, such as carbon, nitrogen, phosphorus, arsenic, antimony etc. could also take place. Various electrode potentials, relative to E_{Na} = 0 V, at 700°C in fused chloride melts containing calcium chloride, are as follows:



[0024] The metal compound or semi-metal compound can be in the form of single crystals or slabs, sheets, wires, tubes, etc. In addition, the metal oxide may also be applied to a metal substrate prior to treatment, e.g. TiO₂ may be applied to steel and subsequently reduced to the titanium metal.

[0025] In the present invention, it is important that the potential of the cathode is maintained and controlled potentiostatically so that only oxygen ionisation occurs and not the more usual deposition of the cations in the fused salt.

[0026] Once removal of oxygen from a metal oxide is progressing, the extent to which the reaction occurs depends upon the diffusion of the oxygen in the surface of the metal cathode. If the rate of diffusion is low, the reaction soon becomes polarised and, in order for the current to keep flowing, the potential becomes more cathodic and the next competing cathodic reaction will occur, i.e. the deposition of the cation from the fused salt electrolyte. However, if the process is allowed to take place at elevated temperatures, the diffusion and ionisation of the oxygen dissolved in the cathode will be sufficient to satisfy the applied currents, and oxygen will be removed from the cathode. This will continue until the potential becomes more cathodic, due to the lower level of dissolved oxygen in the metal, until the potential equates to the discharge potential for the cation from the electrolyte.

[0027] The process for carrying out the invention may advantageously be more direct and cheaper than the more usual reduction and refining processes used currently.

[0028] In an alternative embodiment, the invention may thus advantageously provide a method for removing a substance (X) from a solid metal or semi-metal compound (M¹X) by electrolysis in a fused salt (M²Y) or a mixture of salts, which comprises conducting the elec-

trolysis under conditions such that reaction of X rather than M^2 deposition occurs at a surface of an electrode comprising the solid compound, and that X dissolves in the electrolyte M^2Y .

Description of Specific Embodiments

[0029] Embodiments of the invention will now be described, with reference to the drawings, in which;

Figure 1 is a schematic illustration of the apparatus used in the present invention; and

Figure 2 illustrates the difference in currents for electrolytic reduction of TiO_2 pellets under different conditions.

[0030] Figure 1 and the following description of figure 1 relate to the removal of oxygen dissolved in metallic titanium, whereas the subsequent Examples all relate to electro-reduction of metal compounds. However, the cell arrangement used in the Examples is substantially the same as in figure 1, with an electrode comprising the metal compound substituted for the metallic cathode.

[0031] Figure 1 shows a piece of titanium made the cathode in a cell consisting of an inert anode immersed in a molten salt. The titanium may be in the form of a rod, sheet or other artefact. If the titanium is in the form of swarf or particulate matter, it may be held in a mesh basket. On the application of a voltage via a power source, a current will not start to flow until balancing reactions occur at both the anode and cathode. At the cathode, there are two possible reactions, the discharge of the cation from the salt or the ionisation and dissolution of oxygen. The latter reaction occurs at a more positive potential than the discharge of the metal cation and, therefore, will occur first. However, for the reaction to proceed, it is necessary for the oxygen to diffuse to the surface of the titanium and, depending on the temperature, this can be a slow process. For best results it is, therefore, important that the reaction is carried out at a suitably elevated temperature, and that the cathodic potential is controlled, to prevent the potential from rising and the metal cations in the electrolyte being discharged as a competing reaction to the ionisation and dissolution of oxygen into the electrolyte. This can be ensured by measuring the potential of the titanium relative to a reference electrode, and prevented by potentiostatic control so that the potential never becomes sufficiently cathodic to discharge the metal ions from the fused salt.

[0032] The electrolyte must consist of salts which are preferably more stable than the equivalent salts of the metal which is being refined and, ideally, the salt should be as stable as possible to remove the oxygen to as low as concentration as possible. The choice includes the chloride salts of barium, calcium, cesium, lithium, strontium and yttrium. The melting and boiling points of these chlorides are given below:

	Melting Point (°C)	Boiling Point (°C)
BaCl ₂	963	1560
CaCl ₂	782	>1600
CsCl	645	1280
LiCl	605	1360
SrCl ₂	875	1250
YCl ₃	721	1507

[0033] It is possible to use mixtures of these salts if a fused salt melting at a lower temperature is required, e. g. by utilising a eutectic or near-eutectic mixture. It is also advantageous to have, as an electrolyte, a salt with as wide a difference between the melting and boiling points as possible, since this gives a wide operating temperature without excessive vaporisation. Furthermore, the higher the temperature of operation, the greater will be the diffusion of the oxygen in the surface layer and therefore the time for deoxidation to take place will be correspondingly less. Any salt could be used provided the oxide of the cation in the salt is more stable than the oxide of the metal to be purified.

[0034] The following Examples illustrate the invention. In particular, Examples 1 and 2 relate to removal of oxygen from an oxide.

Example 1

[0035] A white TiO_2 pellet, 5mm in diameter and 1mm in thickness, was placed in a titanium crucible filled with molten calcium chloride at 950°C. A potential of 3V was applied between a graphite anode and the titanium crucible. After 5h, the salt was allowed to solidify and then dissolved in water to reveal a black/metallic pellet. Analysis of the pellet showed that it was 99.8% titanium.

[0036] Example 2 shows a slip-cast technique for the fabrication of the oxide electrode.

Example 2

[0037] A TiO_2 powder (anatase, Aldrich, 99.9+% purity; the powder possibly contains a surfactant) was mixed with water to produce a slurry ($TiO_2:H_2O = 5:2$ wt) that was then slip-cast into a variety of shapes (round pellets, rectangular blocks, cylinders, etc) and sizes (from millimetres to centimetres), dried in room/ambient atmosphere overnight and sintered in air, typically for two hours at 950°C in air. The resultant TiO_2 solid has a workable strength and a porosity of 40-50%. There was notable but insignificant shrinkage between the sintered and unsintered TiO_2 pellets.

[0038] 0.3g~10g of the pellets were placed at the bottom of a titanium crucible containing a fresh $CaCl_2$ melt (typically 140g). Electrolysis was carried out at 3.0V (between the titanium crucible and a graphite rod anode) and 950°C under an argon environment for 5~15 hours.

It was observed that the current flow at the beginning of the electrolysis increased nearly proportionally with the amount of the pellets and followed roughly a pattern of 1 g TiO_2 corresponding to 1 A initial current flow.

[0039] It was observed that the degree of reduction of the pellets can be estimated by the colour in the centre of the pellet. A more reduced or metallised pellet is grey in colour throughout, but a lesser reduced pellet is dark grey or black in the centre. The degree of reduction of the pellets can also be judged by placing them in distilled water for a time from a few hours to overnight. The partially reduced pellets automatically break into fine black powders while the metallised pellets remain in the original shape. It was also noticed that even for the metallised pellets, the oxygen content can be estimated by the resistance to pressure applied at room temperature. The pellets became a grey powder under the pressure if there was a high level of oxygen, but a metallic sheet if the oxygen levels were low.

[0040] Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) investigation of the pellets revealed considerable differences in both composition and structure between metallised and partially reduced pellets. In the metallised case, the typical structure of dendritic particles was always seen, and no or little oxygen was detected by EDX. However, the partially reduced pellets were characterised by crystallites having a composition of $\text{Ca}_x\text{Ti}_y\text{O}_z$ as revealed by EDX.

Example 3

[0041] It is highly desirable that the electrolytic extraction be performed on a large scale and the product removed conveniently from the molten salt at the end of the electrolysis. This may be achieved for example by placing the TiO_2 pellets in a basket-type electrode.

[0042] The basket was fabricated by drilling many holes (~3.5 mm diameter) into a thin titanium foil (~1.0 mm thickness) which was then bent at the edge to form a shallow cuboid basket with an internal volume of $15 \times 45 \times 45 \text{ mm}^3$. The basket was connected to a power supply by a Kanthal wire.

[0043] A large graphite crucible (140 mm depth, 70 mm diameter and 10 mm wall thickness) was used to contain the CaCl_2 melt. It was also connected to the power supply and functioned as the anode. Approximately 10g slp-cast TiO_2 pellets/blobs (each was about 10 mm diameter and 3 mm maximum thickness) were placed in the titanium basket and lowered into the melt. Electrolysis was conducted at 3.0V, 950°C , for approximately 10 hours before the furnace temperature was allowed to drop naturally. When the temperature reached about 800°C , the electrolysis was terminated. The basket was then raised from the melt and kept in a water-cooled upper part of the Inconel tube reactor until the furnace temperature dropped to below 200°C before being taken out for analysis.

[0044] After acidic leaching (HCl , $\text{pH} < 2$) and washing

in water, the electrolysed pellets exhibited the same SEM and EDX features as observed above. Some of the pellets were ground into a powder and analysed by thermo-gravimetry and vacuum fusion elemental analysis. The results showed that the powder contained about 20,000 ppm oxygen.

[0045] SEM and EDX analysis showed that, apart from the typical dendritic structure, some crystallites of CaTiO_x ($x < 3$) were observed in the powder which may be responsible for a significant fraction of the oxygen contained in the product. If this is the case, it is expected that upon melting the powder, purer titanium metal ingot can be produced.

[0046] An alternative to the basket-type electrode is the use of a "lolly" type TiO_2 electrode. This is composed of a central current collector and on top of the collector a reasonably thick layer of porous TiO_2 . In addition to reducing the surface area of the current collector, other advantages of using a lolly-type TiO_2 electrode include: firstly, that it can be removed from the reactor immediately after electrolysis, saving both processing time and CaCl_2 ; secondly, and more importantly, the potential and current distribution and therefore current efficiency can be improved greatly.

Example 4

[0047] A slurry of Aldrich anatase TiO_2 powder was slp cast into a slightly tapered cylindrical lolly (~20 mm length) comprising a titanium metal foil (0.6 mm thickness, 3 mm width and ~40 mm length) in the centre. After sintering at 950°C , the lolly was connected electrically at the end of the titanium foil to a power supply by a Kanthal wire. Electrolysis was carried out at 3.0V and 950°C for about 10 hours. The electrode was removed from the melt at about 800°C , washed and leached by weak HCl acid ($\text{pH} 1-2$). The product was then analysed by SEM and EDX. Again, a typical dendritic structure was observed and no oxygen, chlorine and calcium could be detected by EDX.

[0048] The slp-cast method may be used to fabricate large rectangular or cylindrical blocks of TiO_2 that can then be machined to an electrode with a desired shape and size suitable for industrial processing. In addition, large reticulated TiO_2 blocks, e.g. TiO_2 foams with a thick skeleton, can also be made by slp casting, and this will help the draining of the molten salt.

[0049] The fact that there is little oxygen in a dried fresh CaCl_2 melt suggests that the discharge of the chloride anions must be the dominant anodic reaction at the initial stage of electrolysis. This anodic reaction will continue until oxygen anions from the cathode transport to the anode. The reactions can be summarised as follows:

anode	$\text{Cl}^- \rightleftharpoons \frac{1}{2}\text{Cl}_2 \uparrow + \text{e}^-$
cathode	$\text{TiO}_2 + 4\text{e}^- \rightleftharpoons \text{Ti} + 2\text{O}^{2-}$
total	$\text{TiO}_2 + 4\text{Cl}^- \rightleftharpoons \text{Ti} + 2\text{Cl}_2 \uparrow + 2\text{O}^{2-}$

[0050] When sufficient O^{2-} ions are present the anodic reaction becomes:



and the overall reaction:



[0051] Apparently the depletion of chloride anions is irreversible and consequently the cathodically formed oxygen anions will stay in the melt to balance the charge, leading to an increase of the oxygen concentration in the melt. Since the oxygen level in the titanium cathode is in a chemical equilibrium or quasi-equilibrium with the oxygen level in the melt for example via the following reaction:



[0052] It is expected that the final oxygen level in the electrolytically extracted titanium cannot be very low if the electrolysis proceeds in the same melt with controlling the voltage only.

[0053] This problem can be solved by (1) controlling the initial rate of the cathodic oxygen discharge and (2) reducing the oxygen concentration of the melt. The former can be achieved by controlling the current flow at the initial stage of the electrolysis, for example gradually increasing the applied cell voltage to the desired value so that the current flow will not go beyond a limit. This method may be termed "double-controlled electrolysis". The latter solution to the problem may be achieved by performing the electrolysis in a high oxygen level melt first, which reduces TiO_2 to the metal with a high oxygen content, and then transferring the metal electrode to a low oxygen melt for further electrolysis. The electrolysis in the low oxygen melt can be considered as an electrolytic refining process and may be termed "double-melt electrolysis".

[0054] Example 5 illustrates the use of the "double-melt electrolysis" principle.

Example 5

[0055] A TiO_2 lolly electrode was prepared as described in Example 4. A first electrolysis step was carried out at 3.0V, 950°C overnight (~12 hours) in re-melted $CaCl_2$ contained within an alumina crucible.

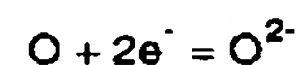
[0056] A graphite rod was used as the anode. The lolly electrode was then transferred immediately to a fresh $CaCl_2$ melt contained within a titanium crucible. A second electrolysis was then carried out for about 8 hours at the same voltage and temperature as the first electrolysis, again with a graphite rod as the anode. The lolly

electrode was removed from the reactor at about 800°C, washed, acid leached and washed again in distilled water with the aid of an ultrasonic bath. Again both SEM and EDX confirmed the success in extraction.

5 [0057] Thermo-weight analysis was applied to determine the purity of the extracted titanium based on the principle of re-oxidation. About 50 mg of the sample from the lolly electrode was placed in a small alumina crucible with a lid and heated in air to 950°C for about 1 hour.
10 The crucible containing the sample was weighted before and after the heating and the weight increase was observed. The weight increase was then compared with the theoretical increase when pure titanium is oxidised to titanium dioxide. The result showed that the sample
15 contained 99.7+-% of titanium, implying less than 3000 ppm oxygen.

Example 6

20 [0058] The principle of this invention can be applied not only to titanium but also other metals and their alloys. A mixture of TiO_2 and Al_2O_3 powders (5:1 wt) was slightly moistened and pressed into pellets (20 mm diameter and 2 mm thickness) which were later sintered in air at
25 950°C for 2 hours. The sintered pellets were white and slightly smaller than before sintering. The pellets were electrolysed in the same way as described in Example 1 and as follows. Pellets were made the cathode in a molten calcium chloride melt, with a carbon anode. Potentials of 2.8V, 3V, 3.1V and 3.3V were applied for 3h
30 at 950°C followed by 1.5h at 800°C. The decomposition potential of pure calcium chloride at these temperatures is 3.2 V. When polarisation losses and resistive losses are considered, a cell potential of around 3.5V is required to deposit calcium. Since it is not possible for calcium to be deposited below this potential, these results
35 prove that the cathodic reaction is:



40 [0059] SEM and EDX analysis revealed that after electrolysis the pellets changed to the Ti-Al metal alloy although the elemental distribution in the pellet was not uniform: the Al concentration was higher in the central part of the pellet than near the surface, varying from 12 wt% to 1 wt%. The microstructure of the Ti-Al alloy pellet was similar to that of the pure Ti pellet.

45 [0060] Figure 2 shows the comparison of currents for the electrolytic reduction of TiO_2 pellets under different conditions. It can be shown that the amount of current flowing is directly proportional to the amount of oxide in the reactor. More importantly, it also shows that the current decreases with time and therefore it is probably the oxygen in the dioxide that is ionising and not the deposition of calcium. If calcium was being deposited, the current should remain constant with time.
55

Claims

1. A method for removing a substance (X) from a solid compound (M¹X) between the substance and a metal or semi-metal (M¹) comprising the steps of; 5

arranging an electrode comprising the solid compound in an electrolyte (M²Y) comprising a fused salt or a mixture of salts, including one or more cations (M²);

arranging an anode in the electrolyte; and

applying a voltage between the electrode and the anode such that the potential at the electrode is lower than a deposition potential for the cation (M²), or the lowest deposition potential for any of the cations (M²), at a surface of the electrode and such that the substance (X) dissolves in the electrolyte. 10
2. A method according to claim 1, in which the compound (M¹X) is an insulator and is used in contact with a conductor. 20
3. A method according to any preceding claim, in which electrolysis is carried out at a temperature of 700°C - 1000°C. 25
4. A method according to any preceding claim, in which the one or more cations (M²) include(s) one or more of Ca, Ba, Li, Cs or Sr and the electrolyte comprises one or more anions (Y), the anion or one of the anions being Cl. 30
5. A method according to any preceding claim, in which the substance (X) comprises O, S, C or N. 35
6. A method according to any preceding claim, in which the metal or semi-metal (M¹) comprises Ti.
7. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Si. 40
8. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Ge. 45
9. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Zr.
10. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Hf. 50
11. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Sm.
12. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises U. 55
13. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Al.
14. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Mg.
15. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Nd.
16. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Mo.
17. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Cr.
18. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) comprises Nb.
19. A method according to any of claims 1 to 5, in which the metal or semi-metal (M¹) produced by the method comprises, or is an alloy of, one or more of Ti, Si, Ge, Zr, Hf, Sm, U, Al, Mg, Nd, Mo, Cr or Nb.
20. A method according to any preceding claim, in which the compound (M¹X) is in the form of a porous pellet or a powder.
21. A method according to any preceding claim, in which a further metal compound or semi-metal compound is present, and the product of the method is an alloy of the metals and/or semi-metals.
22. A method according to any preceding claim, in which the electrode is formed from the solid compound in powdered form by slip-casting and/or sintering.
23. A method according to any preceding claim, in which the current flow at an initial stage of electrolysis is controlled so that current flow during electrolysis does not exceed a predetermined limit.
24. A method according to any preceding claim, in which electrolysis is carried out in two stages, the electrolyte provided in a second stage containing a lower concentration of the substance (X) than an electrolyte provided in a previous stage.
25. A method according to any preceding claim, in which the compound (M¹X) is applied to a metal substrate prior to treatment.
26. A method according to any preceding claim, comprising conducting the electrolysis under conditions such that reaction of the substance (X) rather than deposition of the cation (M²) or any of the cations (M²) occurs at the electrode surface.
27. A method for forming an alloy of two or more com-

ponents (M^1 , M^N), each being a metal or a semi-metal, comprising the steps of;

providing solid compounds (M^1X , M^NZ) of each of the components with another substance or substances (X, Z);
 mixing the solid compounds together;
 providing an electrolyte (M^2Y) comprising a fused salt or a mixture of salts, including one or more cations (M^2);
 arranging a cathode comprising the mixed solid compounds in contact with the electrolyte;
 arranging an anode in contact with the electrolyte; and
 applying a voltage between the cathode and the anode such that the potential at the cathode is lower than a deposition potential for the cation, or the lowest deposition potential for any of the cations, at a surface of the cathode and such that the substance or substances dissolve (s) in the electrolyte.

28. A method according to claim 27, in which the mixed solid compounds are sintered before being contacted with the electrolyte.

29. A method according to claim 27 or 28, comprising conducting the electrolysis under conditions such that reaction of the substance or substances rather than deposition of the cation or any of the cations occurs at the cathode surface.

Patentansprüche

1. Verfahren zum Entfernen einer Substanz (X) von einer festen Verbindung (M^1X) zwischen der Substanz und einem Metall oder Halbmetall (M^1), umfassend die folgenden Schritte:

Anordnen einer die feste Verbindung umfassenden Elektrode in einem Elektrolyt (M^2Y), umfassend eine Salzschnmelze oder ein Gemisch von Salzen, einschließlich einem oder mehreren Kationen (M^2);
 Anordnen einer Anode in dem Elektrolyt; und
 Anlegen einer Spannung zwischen der Elektrode und der Anode, so dass das Potential an der Elektrode niedriger ist als das Abscheidungs-potential für das Kation (M^2) oder das niedrigste Abscheidungs-potential für eines der Kationen (M^2) auf einer Oberfläche der Elektrode und so, dass sich die Substanz (X) in dem Elektrolyt auflöst.

2. Verfahren nach Anspruch 1, bei dem die Verbindung (M^1X) ein Isolator ist und in Kontakt mit einem Leiter verwendet wird.

3. Verfahren nach einem der vorherigen Ansprüche, bei dem Elektrolyse bei einer Temperatur zwischen 700°C und 1000°C durchgeführt wird.

4. Verfahren nach einem der vorherigen Ansprüche, bei dem die ein oder mehreren Kationen (M^2) Ca, Ba, Li, Cs und/oder Sr beinhaltet/beinhalten und der Elektrolyt ein oder mehrere Anionen (Y) umfasst, wobei das Anion oder eines der Anionen Cl ist.

5. Verfahren nach einem der vorherigen Ansprüche, bei dem die Substanz (X) O, S, C oder N umfasst.

6. Verfahren nach einem der vorherigen Ansprüche, bei dem das Metall oder Halbmetall (M^1) Ti umfasst.

7. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Si umfasst.

8. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Ge umfasst.

9. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Zr umfasst.

10. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Hf umfasst.

11. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Sm umfasst.

12. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) U umfasst.

13. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Al umfasst.

14. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Mg umfasst.

15. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Nd umfasst.

16. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Mo umfasst.

17. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Cr umfasst.

18. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Metall oder Halbmetall (M^1) Nb umfasst.

19. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das mit dem Verfahren erzeugte Metall oder Halbmetall (M^1) Ti, Si, Ge, Zr, Hf, Sm, U, Al, Mg, Nd, Mo, Cr und/oder Nb umfasst oder eine Legierung aus einem oder mehreren davon ist.

20. Verfahren nach einem der vorherigen Ansprüche, bei dem die Verbindung (M^1X) in der Form eines porösen Pellets oder eines Pulvers vorliegt.
21. Verfahren nach einem der vorherigen Ansprüche, bei dem eine weitere Metallverbindung oder Halbm-
metallverbindung vorliegt und das Produkt des Ver-
fahrens eine Legierung aus den Metallen und/oder
Halbmetallen ist.
22. Verfahren nach einem der vorherigen Ansprüche, bei dem die Elektrode aus der festen Verbindung in pulverisierter Form durch Schlickergießen und/oder Sintern gebildet wird.
23. Verfahren nach einem der vorherigen Ansprüche, bei dem der Stromfluss in einer Anfangsstufe der Elektrolyse so geregelt wird, dass der Stromfluss während der Elektrolyse eine vorbestimmte Grenze nicht überschreitet.
24. Verfahren nach einem der vorherigen Ansprüche, bei dem Elektrolyse in zwei Stufen durchgeführt wird, wobei der in einer zweiten Stufe vorgesehene Elektrolyt eine niedrigere Konzentration der Substanz (X) enthält als ein in einer vorherigen Stufe vorgesehener Elektrolyt.
25. Verfahren nach einem der vorherigen Ansprüche, bei dem die Verbindung (M^1X) vor der Behandlung auf ein Metallsubstrat aufgebracht wird.
26. Verfahren nach einem der vorherigen Ansprüche, umfassend das Durchführen der Elektrolyse unter solchen Bedingungen, dass eine Reaktion der Substanz (X) anstatt der Abscheidung des Kations (M^2) oder eines der Kationen (M^2) auf der Elektrodenoberfläche erfolgt.
27. Verfahren zum Bilden einer Legierung aus zwei oder mehr Komponenten (M^1 , M^N), die jeweils ein Metall oder ein Halbmetall sind, umfassend die folgenden Schritte:

Bereitstellen fester Verbindungen (M^1X , M^NZ) aus jeder der Komponenten mit (einer) anderen Substanz(en) (X, Z);
Mischen der festen Verbindungen miteinander;
Bereitstellen eines Elektrolyts (M^2Y), umfassend eine Salzschnmelze oder ein Gemisch von Salzen, einschließlich einem oder mehreren Kationen (M^2);
Anordnen einer Kathode, die die gemischten festen Verbindungen in Kontakt mit dem Elektrolyt umfasst;
Anordnen einer Anode in Kontakt mit dem Elektrolyt; und
Anlegen einer Spannung zwischen der Katho-

de und der Anode, so dass das Potential an der Kathode niedriger ist als ein Abscheidungspotential für das Kation oder das niedrigste Abscheidungspotential für eines der Kationen auf einer Oberfläche der Kathode, und so, dass sich die Substanz oder Substanzen in dem Elektrolyt auflöst/auflösen.

28. Verfahren nach Anspruch 27, bei dem die gemischten festen Verbindungen vor dem Kontakt mit dem Elektrolyt gesintert werden.
29. Verfahren nach Anspruch 27 oder 28, umfassend die Durchführung der Elektrolyse unter solchen Bedingungen, dass die Reaktion der Substanz oder Substanzen anstatt der Abscheidung des Kations oder eines der Kationen auf der Kathodenoberfläche erfolgt.

Revendications

1. Procédé pour retirer une substance (X) d'un composé solide (M^1X) entre la substance et un métal ou un semi-métal (M^1) comprenant les étapes consistant à :

arranger une électrode comprenant le composé solide dans un électrolyte (M^2Y) comprenant un sel fondu ou un mélange de sels, incluant un ou plusieurs cations (M^2);
arranger une anode dans l'électrolyte; et
appliquer une tension entre l'électrode et l'anode de telle sorte que le potentiel à l'électrode est plus faible qu'un potentiel de dépôt du cation (M^2), ou le potentiel de dépôt le plus faible de l'un quelconque des cations (M^2), au niveau d'une surface de l'électrode et de telle sorte que la substance (X) se dissout dans l'électrolyte.

2. Procédé selon la revendication 1, dans lequel le composé (M^1X) est un isolateur et est utilisé en contact avec un conducteur.
3. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'électrolyse est menée à bien à une température de 700°C - 1000°C.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel un ou plusieurs cations (M^2) comprend/comprennent un ou plusieurs parmi le Ca, Ba, Li, Cs ou Sr, et l'électrolyte comprend un ou plusieurs anions (Y), l'anion ou l'un des anions étant du Cl.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la substance (X) comprend du O, S, C ou N.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le métal ou semi-métal (M^1) comprend du Ti.
7. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Si.
8. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Ge.
9. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Zr.
10. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Hf.
11. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Sm.
12. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du U.
13. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Al.
14. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Mg.
15. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Nd.
16. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Mo.
17. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Cr.
18. Procédé selon l'une quelconque des revendications précédentes 1 à 5, dans lequel le métal ou semi-métal (M^1) comprend du Nb.
19. Procédé selon l'une quelconque des revendications 1 à 5 précédentes, dans lequel le métal ou semi-métal (M^1) produit par le procédé comprend, ou est un alliage de, un ou plusieurs parmi le Ti, Si, Ge, Zr, Hf, Sm, U, Al, Mg, Nd, Mo, Cr ou Nb.
20. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé (M^1X) est sous forme de pastille poreuse ou de poudre.
21. Procédé selon l'une quelconque des revendications précédentes, dans lequel un autre composé métallique ou composé semi-métallique est présent, et le produit du procédé est un alliage des métaux et/ou des semi-métaux.
22. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'électrode est formée avec le composé solide sous forme pulvérisée par coulage en barbotine et/ou frittage.
23. Procédé selon l'une quelconque des revendications précédentes, dans lequel le flux de courant au stade initial de l'électrolyse, est contrôlé de telle sorte que le flux de courant durant l'électrolyse ne dépasse pas une limite prédéterminée.
24. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'électrolyse est menée à bien en deux stades, l'électrolyte fourni à un deuxième stade contenant une concentration plus faible de la substance (X) qu'un électrolyte fourni à un stade antérieur.
25. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé (M^1X) est appliqué à un substrat métallique avant traitement.
26. Procédé selon l'une quelconque des revendications précédentes, comprenant mener à bien l'électrolyse dans des conditions telles que la réaction de la substance (X), plutôt que le dépôt du cation (M^2) ou de l'un quelconque des cations (M^2), survient à la surface de l'électrode.
27. Procédé pour former un alliage de deux ou plusieurs composants (M^1 , M^N), chacun étant un métal ou un semi-métal, comprenant les étapes consistant à :
- fournir des composés solides (M^1X , M^NZ) de chacun des composants avec une autre substance ou substances (X, Z);
- mélanger les composés solides ensemble;
- fournir un électrolyte (M^2Y) comprenant un sel fondu ou un mélange de sels, incluant un ou plusieurs cations (M^2);
- arranger une cathode comprenant les composés solides mélangés, en contact avec l'électrolyte;
- arranger une anode en contact avec l'électrolyte; et
- appliquer une tension entre la cathode et l'anode de telle sorte que le potentiel à la cathode

est plus faible qu'un potentiel de dépôt du cation, ou le potentiel de dépôt le plus faible de l'un quelconque des cations, au niveau d'une surface de la cathode et de telle sorte que la substance ou les substances se dissout/dissolvent dans l'électrolyte. 5

28. Procédé selon la revendication 27, dans lequel les composés solides mélangés sont frittés avant d'être mis en contact avec l'électrolyte. 10

29. Procédé selon la revendication 27 ou 28, comprenant mener à bien l'électrolyse dans des conditions telles que la réaction de la substance ou des substances plutôt que le dépôt du cation ou de l'un quelconque des cations, survient à la surface de la cathode. 15

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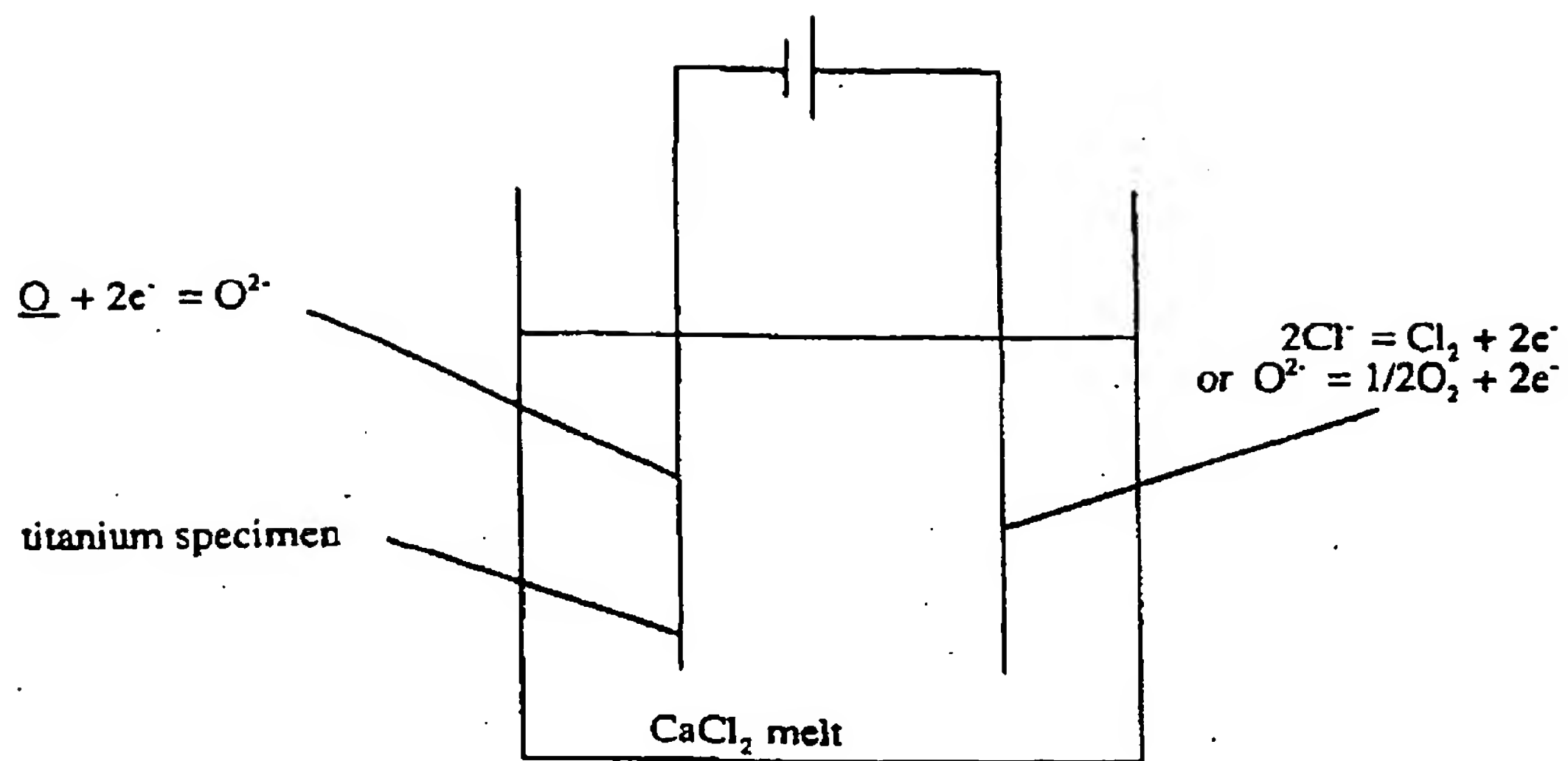


Figure 1

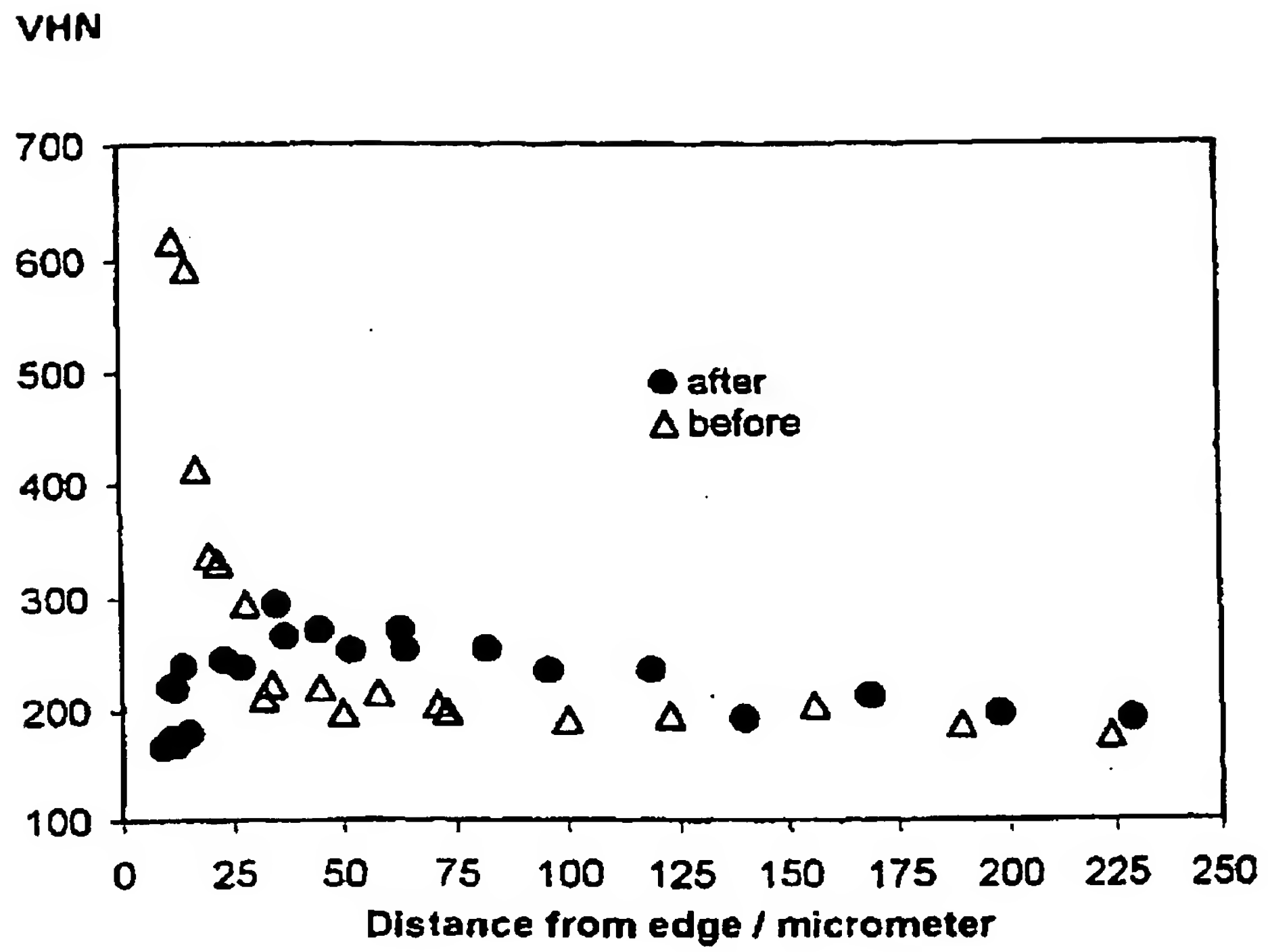


Figure 2